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1302 194

DRAWINGS ATTACHED

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(19)

## (54) MASS SPECTROMETER


(71) We, SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ N.V., a company organized under the laws of the Netherlands, of 30 Carel van Bylandtlaan, The Hague, the Netherlands, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—


This invention relates to a time-of-flight mass spectrometer in which ions to be separated, on their way from an ion source to an ion collector, pass through an electrostatic field set up between two coaxial cylinder electrodes of which one surrounds the other, while describing helical orbits about the inner electrode.

Time-of-flight mass spectrometers are known and have been commercially available for a number of years, but in these instruments the ion path is straight. It has been proposed to use a helical flight path in a radial electrostatic field between two coaxial cylinder electrodes, into which field the ions are injected tangentially, with the axial component. A helical orbit of a constant radius is then obtaned for all ions for which the centrifugal force balances the force exerted by the radial electrostatic field. This means that all ions which have been accelerated to a particular energy ($eU_1$) will describe such an orbit, independent of their mass and charge.

The passage of ions through a radial electric field results in the following improvements (some of which are already known):

1. the flight path of the ions is increased giving an increase in resolution;
2. energy focusing takes place in the radial electric field, this may be used to further increase resolution;
3. spatial refocusing takes place in the radial electric field, giving an increase in sensitivity;
4. the background current is reduced because the collector is no longer in line with the ion gun. This effectively increases the sensitivity.

The practical realization of a helical time-of-flight mass spectrometer raises many problems which are related to the known theoretical conditions that the ions should only experience a truly radial field and should be injected tangentially into this field. Additional conditions are:

1. Fringing field produced by the radial electric field should be kept at a minimum.
2. The pitch of the helix described by the orbiting ions must be such that adjacent turns of the orbit do not interfere with each other.

Furthermore, if full use is to be made of the focusing properties of the radial electric field then, in addition to the above conditions required for stable orbits, the following conditions must be met as well:

(i) For optimum refocusing the angle of deflection through the radial electric field must be $n\pi/\sqrt{2}$ where n is an integer.

(ii) For maximum energy resolution the angle of deflection through the radial electric field must be $(2n-1)\pi/\sqrt{2}$ where n is an integer.

(iii) Entrance and exit apertures must be used depending on the energy resolution required.

From these conditions we see that the most critical stages in the flight path of ions in a helical time-of-flight mass spectrometer concern the entry of the ions into the field between the cylinder electrodes and, to a lesser degree the exit from this field.

The invention provides the means for overcoming the problems related to the above-mentioned conditions.

According to the invention, a mass spectrometer is provided comprising means for sending ions in the direction of a point (34) situated between corresponding portions (32—33) of the end faces of the electrodes (17, 18) at one end thereof, which direction


[*Price 25p*]

is perpendicular to the radius from the electrode axis to the said point 34 and has an axial component, the said end face portions lying in a plane through the point 34 which is at least approximately perpendicular to the said direction.

Corresponding portions (42—43) of the end faces of the cylinder electrodes at the other end thereof may lie in a plane, which intersects the common electrode axis at substantially the same angle $\beta$ as does the plane mentioned in the immediately preceding paragraph and which contains a point (35) situated between the two end face portions 42—43 at which this plane intersects a helix about the common axis at a substantially right angle.

Important advantages can be obtained by means of a diaphragm electrodes (20 and/or 22) each facing two corresponding end face portions (32—33 and/or 42—43, respectively) at a relatively short distance d. Preferably, electrically conductive grids (21 and/or 23), electrically connected to the diahragm electrodes, cover the openings therein, while permitting the passage of ions. Tungsten mesh is conveniently used for these grids.

The invention is further described by way of example with reference to the accompanying drawings wherein:

figures 1A to 1E show the basic components of a mass spectrometer in accordance with the present invention schematically and in different views;

figure 2 shows the electrical circuit diagram of the mass spectrometer of figure 1; and

figures 3 to 6 show typical oscilloscope displays produced with a mass spectrometer according to figure 1.

Turning now to Figure 1, the spectrometer comprises an ion gun indicated generally by reference 1, an electrostatic analyzer assembly 16 which provides the radial electric field and a collector indicated by reference 24.

The ion gun 1 comprises an ion source 2 and a cathode ray tube structure 3. The ion source comprises an ionization chamber 4 provided with an inlet 6 for a gaseous sample. In the chamber 4, a filament 5 and an electron trap 8 serve to create a stream of electrons, and a repeller plate 7 serves to drive ions formed by electron bombardment out of chamber 4. (The numerals 5, 7 and 8 point to the electrical terminals of the respective parts.) After having passed through an accelerator electrode 9, a focusing electrode 10 and an astigmatism control electrode 11 — which electrodes are parts of the structure 3 — the ions form a narrow beam of accelerated ions. This beam can be deflected in two mutually perpendicular directions (the Y- and X-directions) by two pairs of deflection electrodes 12, 30 (the "Y-plates") and 15, 31 (the "X-plates"). The cathode ray tube structure further comprises a geometry control electrode 13 surrounded by a stainless steel cylinder 14.

The electrostatic analyzer assembly 16 comprises an outer cylinder electrode 17 and an inner cylinder electrode 18 which are coaxial. The end faces (also referred to as "edges") of these electrodes each have a predominantly axial portion and a predominantly circumferential portion. The following references will be used for both cylinders: 32—33 for the predominantly axial portion(s) and 33—32 for the predominantly circumferential portion(s) at the left hand side; 42—43 for the predominantly axial portion(s) and 43—42 for the predominantly circumferential portion(s) at the right hand side in the drawing. In order not to complicate Fig. 1B unduly the rear parts of the circumferential portions 33—32 and 43—42 are not shown. A diaphragm electrode 20 is situated at a relatively small distance d from the end face portions 32—33. The opening (or "slit") of this electrode is covered by a grid 21 adjacent to electrode 20 at that side, which faces edge portions 32—33. Similarly a diaphragm electrode 22 is situated at a distance d from edge portions 42—43, its opening (or "slit") being covered by a grid 23. Each of the grids is a 90% transparent tungsten mesh.

The collector 24, an electron multiplier, comprises an entrance grid 25, a cathode 26, a dynode strip 27, a field strip 28 and an anode 29. A signal representing the current of ions arriving at the collector is taken from anode 29 and supplied to a cathode ray tube oscilloscope 41 (in figure 2) or to some other device for recording or visually displaying this signal.

By sweeping the ion beam across the opening in diaphragm electrode 20, the ion gun causes a group of ions to enter the space between cylinder electrodes 17 and 18. The ions of this group can be considered to have a common starting point, somewhere between the deflection electrodes of that pair (12, 30 or 15, 31) which is used for sweeping the ion beam across the opening in diaphragm electrode 20. Differences in velocity between ions of different kinds cause the ions in a group to arrive at the collector at different instances and, hence, to produce a spectrum or oscilloscope 41.

Except for the presence of the analyzer assembly 16 and alternations to the flight path of the ions, the mass spectrometer of figures 1 and 2 is very similar to the instrument described in copending application No. 20005/69 (Serial No. 1302193). It is emphasized, however, that the electrostatic analyzer assembly may also be used with other types of ion gun and/or collector. Hence, the invention is not restricted to mass spectro-

meters having the particular ion gun and/or collector shown in figures 1A, 1B and 1C.

Turning now to the flight path the ions actually follow in this particular instrument. Figures 1A and 1B show a path from the Y-deflection plates 12 and 30 to the opening in diaphragm electrode 20, which path is straight except for a deflection between the plates 15 and 31. Figure 1B shows that the ions next follow a helical path of a radius $R_o$ between cylinders 17 and 18.

The helical motion of the ions starts at a point 34 just after the ions have passed through the diaphragm electrode 20. The helical motion of the ions stops at 35 just before the ions pass through the diaphragm electrode 22. The total flight path of the ions is from the Y-deflection plates 12 and 30 through the geometry control electrode 13 passing between the X-deflection plates 15 and 31, through diaphragm electrode 20, through grid 21 and into the electrostatic analyzer, spiralling from 34 to 35 between cylinders 17 and 18 next passing through grid 23, through diaphragm electrode 22, through the entrance grid 25 of the electron multiplier 24, on to the cathode 26 of the electron multiplier 24. The last steps are also shown in Figure 1C.

Turning now in more detail to the design of the electrostatic analyzer assembly. The design is such that the ion beam is not exposed to the radial electric field until the ions actually arrive at 34 in the electric field (see figures 1A and 1B). Furthermore, the radial electric field is established between cylinders 17 and 18 in such a manner that the beam arrives at 34 normal to the electric field. This is done as follows: Firstly, both cylinders 17 and 18 are cut in an approximately straight line between points 32 and 33 which lies in a plane that is at angle $\beta$ with respect to the cylinder axis. The length of this cut is equal to the shortest distance between adjacent turns of the desired helical orbit, or distance $32—33 \cong q \cos \beta$, where q is the pitch of the helix. Secondly, the cylinders are also cut from point 33 to point 32 along the cylinders' circumference. This cut is a helix of radius $R_1$ in cylinder 18 and of radius $R_2$ in cylinder 17. The pitches of both helical cuts are equal to q=pitch of orbital helix. This manner of cutting the cylinders ensures that undesirable fringe effects due to the electric field boundary along the orbital path (i.e. parallel to the orbit) are at least a distance $\frac{1}{2} q \cos \beta$ away from the orbit. This is sufficient to ensure stable orbiting. In the instrument of figure 1, the axis of the ion gun 1 and the common cylinder electrode axis are in the same plane and mutually perpendicular. Hence, the cylinders are mounted in such a fashion that the deflection-angle caused by the X-plates 15, 31 equals $\beta$; in other words the cylinders are displaced towards the right with respect to the ion gun as shown in Figure 1B. Furthermore, both cylinders are rotated anti-clockwise over an angle $\alpha$ so that ion beam to the point 34 is perpendicular to the electrode radius through the point 34. This is shown in Figure 1A. By these adjustments of the cylinders it is ensured that the beam enters normally to the electric field. The angle $\beta$ is directly related to the pitch of the orbital helix, while $\alpha$ is dependent on $R_o$ and the distance from point 34 to the Y-deflection plates 12 and 30. With this way of mounting the ion gun and the cylinders the correct beam angles are obtained with the aid of appropriate non-zero electric fields in between Y-plate 12 and Y-plate 30 and in between X-plate 15 and X-plate 31. Alternatively, the ion gun may be mounted in a position in which its axis passes through 34 at the angles described. In addition to the above-mentioned devices for ensuring a successful injection of the ions into the radial electric field, a further device is needed. This device is the diaphragm electrode 20 and the tungsten grid mesh 21. This entrance diaphragm assembly has six different functions:

1. The width Wy of the aperture in the direction in which the ion beam is swept across it, serves to give the desired ion-bunch duration. In this function the aperture acts identically to slit (reference 4) of the apparatus described in the specification of our co-pending application No. 20005/69 (Serial No. 1302193);

2. The length Wx of the aperture (along the cylinder-axis) serves to limit the beam width. This is important, especially when double differential impulse sweeping is used, because this electrostatic analyzer does not possess any refocusing properties along the cylinder axis (or X-axis). Radial electric fields refocus every 127°, but only in radial direction.

It is to be understood that Wx can also be used to determine the ion bunch duration by either using X-deflection plates for sweeping the beam across the diaphragm or by rotation of the ion-gun over an angle of 90° about its axis, thereby interchanging the Y- and X-axis. Without beam limiting, the ions from adjacent turns of the orbit would interfere with each other towards the end of their travel, i.e. the beam spread or divergence must be kept less than the helical pitch.

3. In conjunction with the diaphragm electrode 22 at the exit it can be used to control the energy resolution of the electrostatic analyzer assembly and thereby the mass spectral resolution of the whole instrument. In this particular instrument the slit apertures used, were such as to give maximum sensitivity with reasonable resolution. It is

to be understood that the apertures in both electrode 20 and electrode 22 can equally well be used to give maximum resolution.

4. To act as a shielding plate. In this function, electrode 20 serves to shield the stray fields produced by the two cylinders, i.e. along edge 32—33 from the ion beam.

5. To act as a shielding plate between the inner surface of the inner cylinder (notice extension of plate 20 into cylinder 18 in figure 1D) and the ion beam. The outer surface of the outer cylinder is shielded by the vacuum chamber.

6. Finally, assemblies 20, 21 and 22, 23 are necessary for sharply defining a particular total deflection angle in the radial field, e.g. an odd multiple of $\pi/\sqrt{2}$.

The technique used here relies on narrowing the fringing fields with the aid of shielding diaphragms and is based on a theory developed by Herzog (R. Herzog, Z. Physik, 97 (1935) 596; R. Herzog, Z. Physik, 41 (1940) 18). Furthermore, an innovation has been added to this technique. In essence, the extension of the fringing fields is controlled by positioning an apertured diaphragm 20 a certain distance d from the analyzer edge 32—33.

Furthermore, a potential, approximately equal to $\frac{1}{2}$ $U_2$ ($U_2$ is the voltage between cylinder electrodes 17 and 18), is applied to this diaphragm. A complication arises in that the separation d is not only dependent on the cylinder gap ($R_2$—$R_1$), but also on the dimensions of aperture in the diaphragm electrode 20 and on the thickness of this electrode. In Herzog's theory two values for d can be derived. One is based on the use of an infinitely thin electrode, the other on the use of an infinitely thick diaphragm. The actual value of d is determined by interpolation between these two extremes. Both values of d converge when the aperture approaches zero. This has been achieved here with the aid of the 90% transparent tungsten mesh 21. This grid mesh leaves nearly the full aperture for the ion beam to get through, but it also closes the diaphragm electrically thereby making d independent of the thickness of the diaphragm. In addition, it offers the advantage that a change in the aperture size does not require a change in d. The gap d was calculated so that the radial electric field terminates at the edge portions 32—33, of cylinder 17 and cylinder 18. The gap d is constant over the whole length of these portions, or in other words, the diaphragm is mounted under angles $\alpha$ and $\beta$ with respect to the X—Y plane.

Thus, we see that the consequences of this technique are that the beam does indeed enter the radial electric field at 34 and normally to this radial electric field. Furthermore, the beam is only exposed to the radial field from point 34 onward and not prior to this point. It should be understood that although the aperture in the diaphragm 20 shown in figure 1D consists of a round hole (i.e. Wx=Wy), it would be advantageous not to have equal width and length if maximum energy resolution is required.

The same reasoning applied to the entrance side of the analyzer can of course equally well be applied to the exit side 35. Ions are made to leave a helical orbit by a technique which is essentially the inverse of the injection technique. Again, the diaphragm (22) is covered with tungsten grid mesh (23). The aperture is chosen to give maximum transmission. In all other respects the extraction side is identical to the injection side.

The total angle of deflection through the radial field must be $n\pi/\sqrt{2}$ where n is an odd integer. In this particular instrument n=17 giving a total deflection angle of 2163.7°. This corresponds to 6 complete revolutions +3.7°. This total deflection angle is built into the analyzer assembly. The exit edge portions 42—43 are shifted 3.7° with respect to the entrance edge portions 32—33. With the assembly rotated over an angle $\alpha$ (see Figure 1A) to satisfy one of the entrance conditions, the exit side will be at an angle $\gamma$ above the horizontal (see Figure 1 C) where $\gamma=\alpha-3.7°$. The electron multiplier 24 is mounted under angles $\beta$ and $\gamma$ to ensure that the ions will hit normal to the cathode 26. The distance between multiplier and analyzer assembly is not critical and it is to be understood that with the aid of shielding plates and/or deflection plates the electron multiplier position can be made quite arbitrary.

Figure 2 shows the complete circuit diagram of this helical time-of-flight mass spectrometer. In this diagram the ion gun 1, the analyzer assembly 16 and the ion collector 24 are represented by blocks. The reference numbers at the edges of these blocks correspond to those used in figure 1.

The power supplies for the ion-gun are provided by power packs indicated generally by the references 36, 37 and 40. More specifically, power pack 37 provides the necessary power for operating the ionization chamber 2 and is kept floating at a high positive potential provided by power pack 36. Power pack 36 provides, in addition to this floating potential, the necessary power to operate the cathode ray tube structure 3. The actual operating voltages are slightly different from those used in provisional specification 20005/69 because the operating conditions are slightly different from those in the co-pending application No. 20005/69 (Serial No. 1302193). More specifically, the ion beam as previously explained needs to be offset in the X- and Y-direction, thus requiring

slightly higher X- and Y-deflection voltages. Furthermore, the focal length under which this ion-gun operates is shorter, therefore requiring slightly different voltages on the rest of the cathode ray tube structure. It was found that optimum focusing occurred with the astigmatism control electrode 11 at a potential of minus 300 volts. This potential was derived from power pack 40 but could equally well have been derived from any suitable negative power supply such as, for example, power pack 38.

Ion bunching is provided by pulse-generator 39, which also supplies the triggering pulse for the oscilloscope 41. Power supply 38 provides the necessary voltages for the collector 24 which is a magnetic electron multiplier. The output of this multiplier is fed to the vertical amplifier of the oscilloscope 41.

The electrostatic analyzer assembly, reference 16 receives its potentials for power pack 40.

There are several different modes of operation for the electrostatic analyzer assembly. Firstly, there is the symmetric mode whereby the inner and outer cylinders are kept at equal but opopsite potentials. For positive ions the inner cylinder would be kept at a negative potential, while the outer cylinder is kept at a positive potential. If the ion accelerator voltage is $U_1$, then the potential between the cylinders must be

$$U_2=2U_1 \mathrm{Ln}\, R_2/R_1.$$

The equipotential between the cylinders must be $R_o=\sqrt{R_1 . R_2}$ would then be approximately zero and this would, therefore, not affect the total ion energy. The entrance and exit diaphragm electrodes are always kept at approximately the orbital equipotential. This holds true whatever the orbital equipotential is. Both the entrance diaphragm potential and the exit diaphragm potential are individually variable, thus allowing one to optimize the performance of the instrument. The second mode of operation is the asymmetric mode. In this mode the potential on the inner and outer cylinders are not equal nor do they have to be of opposite polarity. Under these conditions the orbital equipotential will no longer be zero and the total ion energy will vary in accordance with this equipotential. In this particular instrument optimum performance was achieved with asymmetric operation as shown in Figure 2.

Figure 2 further shows typical operating voltages and these are indicated in brackets.

Figures 3, 4, 5 and 6 show some of the spectra obtained with this instrument. Notice in Figure 3 the lack of background and general sharpnes of the peaks. Figure 4 shows a spectrum of Xenon with all instrument parameters set for maximum sensitivity. A resolution of approximately 300 was obtained. Figure 5 shows a spectrum, again of Xenon, but this time the instrument was adjusted to give maximum resolution (630). Figure 6 shows a spectrum of heptacosafluorotributylamine. Notice the excellent sensitivity (inlet system at room temperature) and good resolution over the whole mass range. The scanning time for this spectrum (m/e=0 to m/e=614) is 50.4 $\mu$ sec.

WHAT WE CLAIM IS:—

1. Time-of-flight mass spectrometer in which ions to be separated, on their way from an ion source to an ion collector, pass through an electrostatic field set up between two coaxial cylinder electrodes of which one surrounds the other, while describing helical orbits about the inner electrode, characterized by means for sending ions in the direction of a point (34) situated between corresponding portions (32—33) of the end faces of the electrodes (17, 18) at one end thereof, which direction is perpendicular to the radius from the electrode axis to the said point 34 and has an axial component, the said end face portions lying in a plane through the point 34 which is at least approximately perpendicular to the said direction.

2. Time-of-flight mass spectrometer according to claim 1, characterized in that corresponding portions (42—43) of the end faces of the cylinder electrodes at the other end thereof lie in a plane, which intersects the common electrode axis at substantially the same angle $\beta$ as does the plane mentioned in claim 1 and which contains a point (35) situated between the two end face portions 42—43 at which this plane intersects a helix about the common axis at a substantially right angle.

3. Time-of-flight mass spectrometer according to claim 2, characterized by a diaphragm electrode 22 which faces the two end face portions 42—43 at a relatively short distance d.

4. Time-of-flight mass spectrometer according to claim 1, 2 or 3, characterized by a diaphragm electrode 20 which faces the end face portions 32—33 at a relatively short distance d.

5. Time-of-flight mass spectrometer according to claim 4, characterized in that the said means for sending ions comprise a source (1) of a beam of accelerated ions which includes at least one pair of deflection electrodes (12, 30 and/or 15, 31) for sweeping the ion beam across the opening of the diaphragm electrode 20.

6. Time-of-flight mass spectrometer according to claim 3, 4 or 5, characterized by voltage supply means capable of maintaining the cylinder electrodes at different potentials and the diaphragm electrode(s) at

an intermediate potential (intermediate potentials).

7. Time-of-flight mass spectrometer according to any one of claims 3 to 6, characterized in that the opening of at least one diaphragm electrode (20, 22) is covered by an electrically conductive grid (21, 23) permitting the passage of ions.

8. Time-of-flight mass spectrometer according to claim 7, characterized in that the grid is adjacent to that side of the diaphragm electrode, which faces the said end face portions of the cylinder electrodes.

9. Time-of-flight mass spectrometer according to claim 7 or 8, characterized in that the grid is a tungsten mesh.

10. Time-of-flight mass spectrometer according to any one of claims 1 to 9, characterized in that the remaining end face portions (viz. those not lying in one of the said planes) are helical and have a pitch equal to the pitch of a helical ion orbit.

11. Time-of-flight mass spectrometer substantially as hereinbefore described with particular reference to figures 1 and 2 of the drawing.

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1302194 COMPLETE SPECIFICATION

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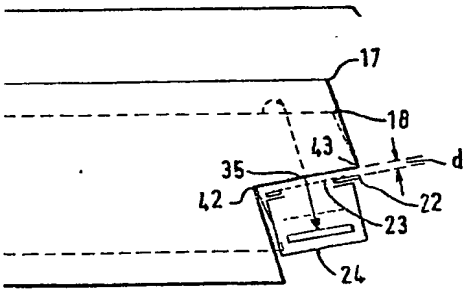



FIG.1C

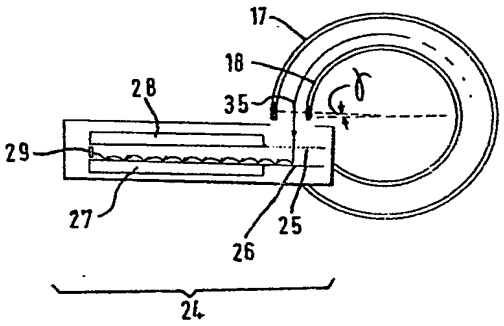
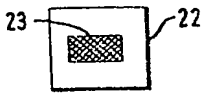



FIG. 1E



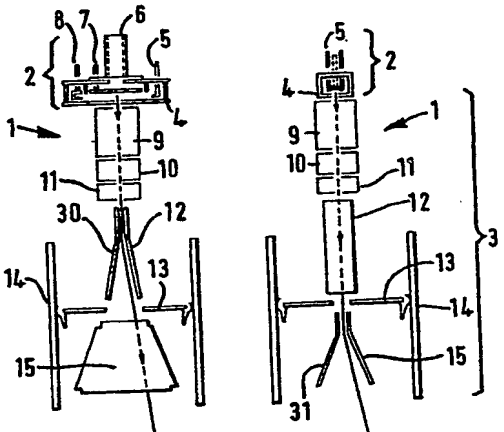
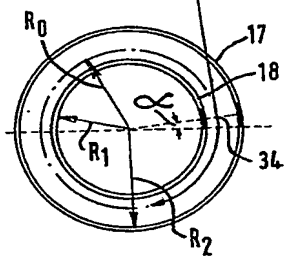
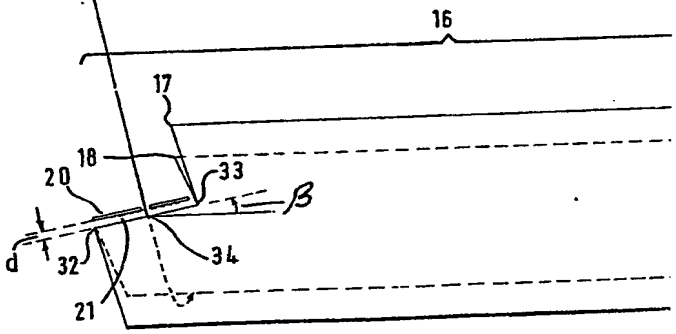



FIG. 1A

FIG. 1B



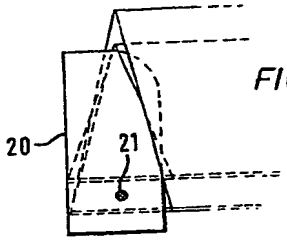




FIG. 1D

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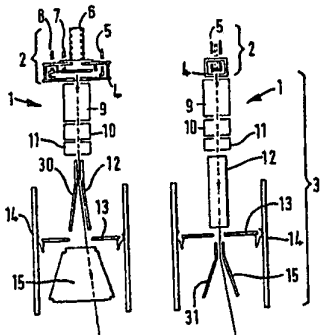



FIG. 1A

FIG. 1B

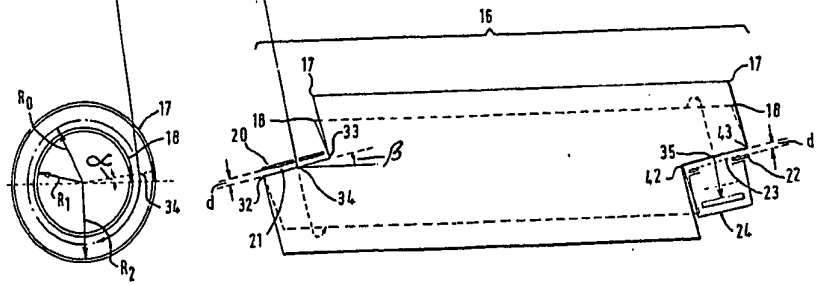
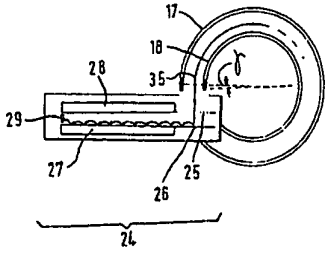



FIG. 1C



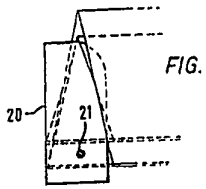




FIG. 1D


FIG. 1E

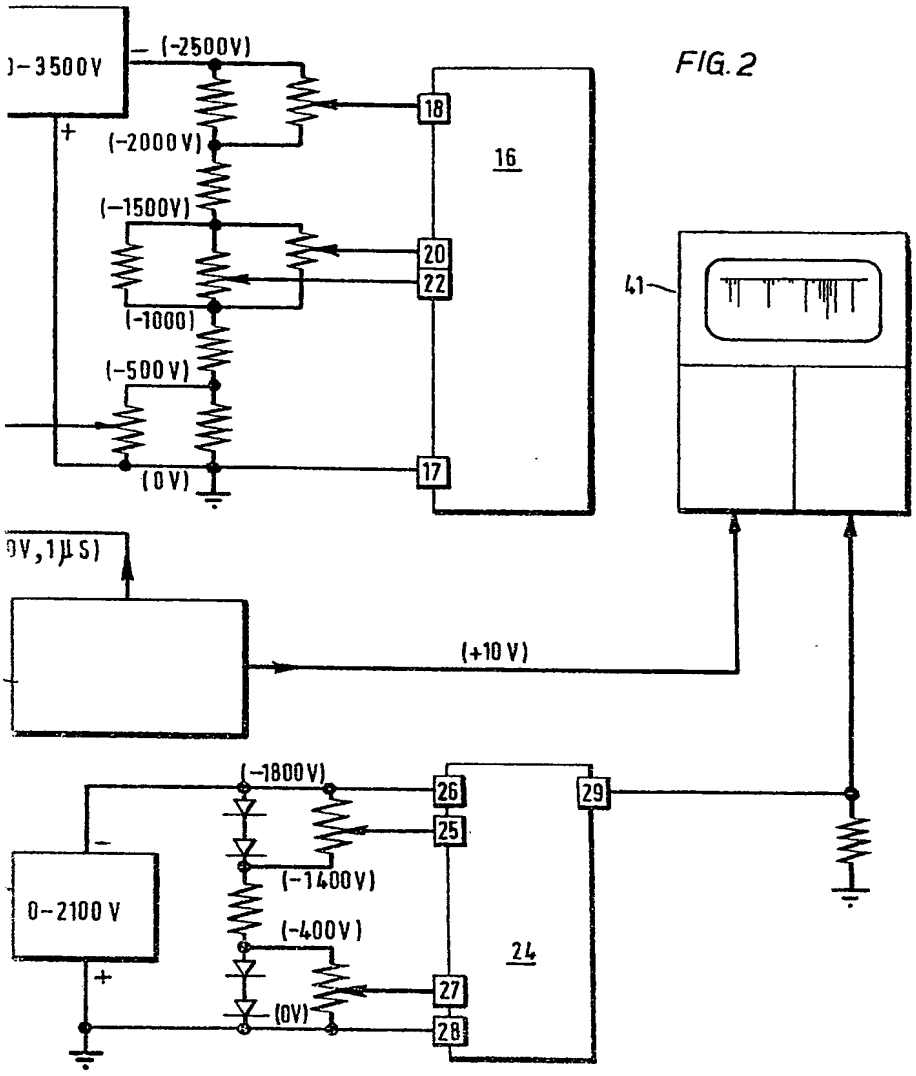
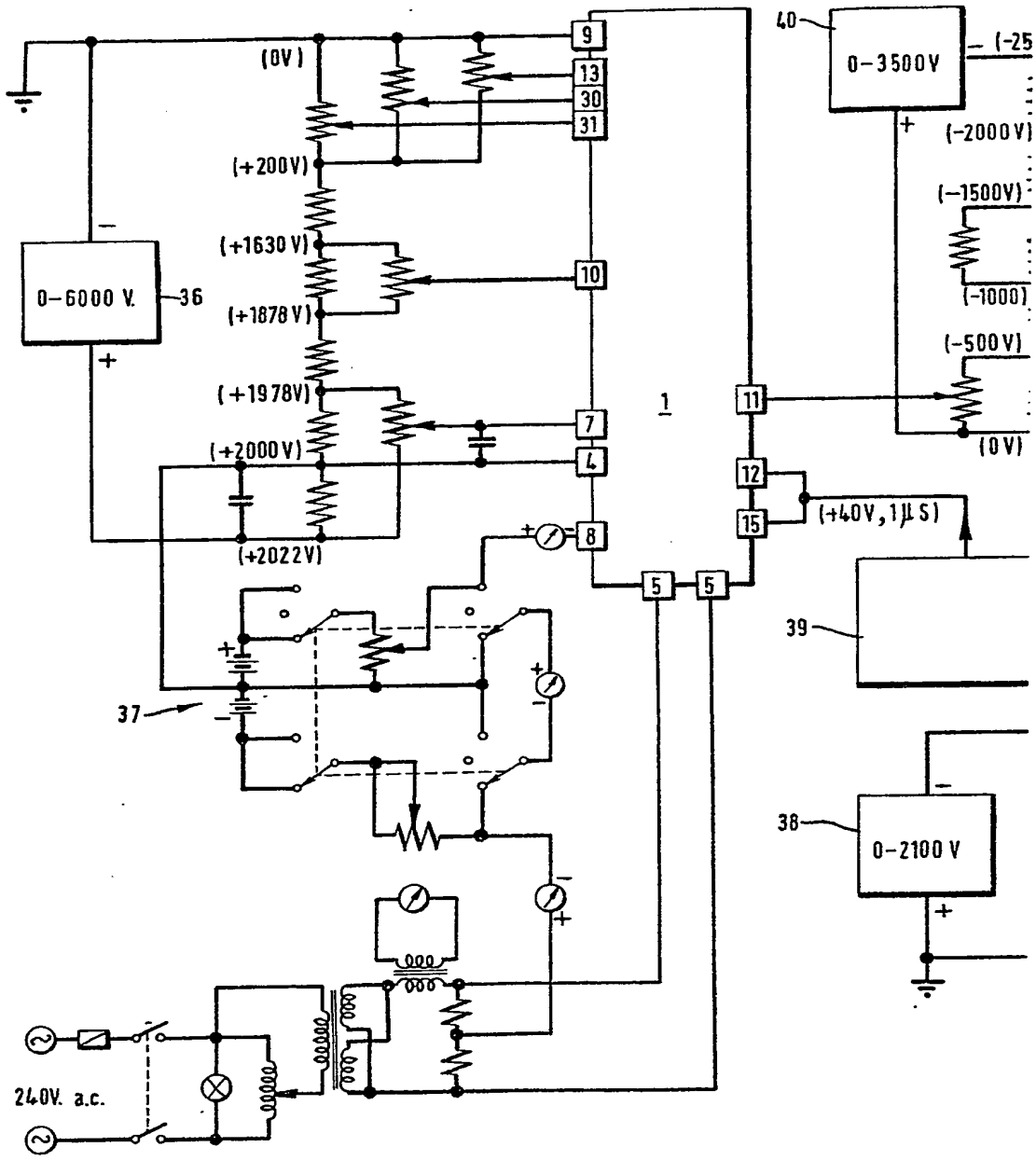



FIG. 2



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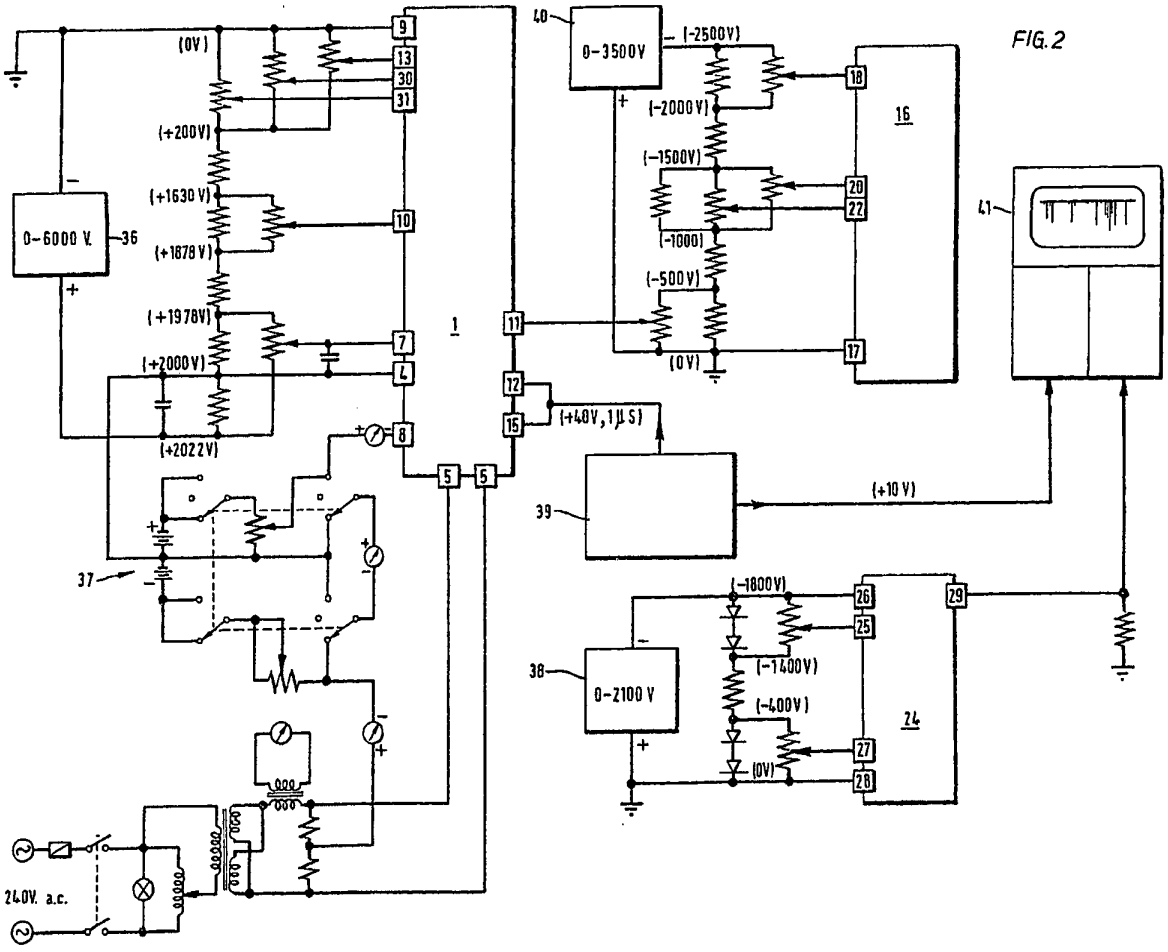
Sheet 2

FIG. 2



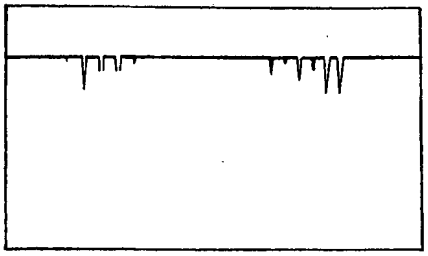


FIG.3

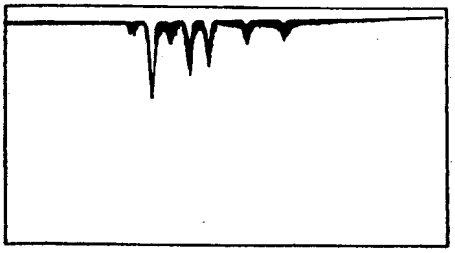


FIG.4

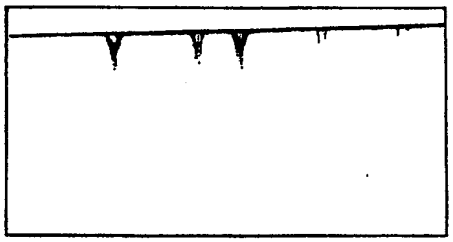


FIG.5

FIG.6